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(54) Title: DIRT ADHESION REDUCTION COATING IN POLYCARBONATE SHEET

(57) Abstract: A transparent or translucent sheet comprising a substrate having on the outer surface facing the atmosphere a coating composition having a hydroxy-functional silicone modified acrylate polymer additive in sufficient amount to allow ease of removing solid particles (dirt) and/or liquids on the surface by reducing the adhesion of such particles and/or liquids to the substrate. The coating composition used for manufacturing the sheet also has in combination therewith an ultra violet absorber along with a polymer matrix such as an acrylate polymer and a solvent such as methoxypropanol and eventually a mar resistant coating. The amount of silicone modifier acrylate polymer may range from about 0.5 to about 6.0 weight % based on the total weight of the coating composition. A preferred ultra violet absorber is a polybenzoylresorcinol. The preferred substrate is a transparent aromatic polycarbonate resin sheet or multiwall polycarbonate at least two polycarbonate sheets having interdisposed there between and joining said sheets a structure of essentially any configuration.

DIRT ADHESION REDUCTION COATING IN POLYCARBONATE SHEET

FIELD OF THE INVENTION

This invention relates to a transparent or translucent sheet comprising a substrate having a coating with a composition comprising an additive that reduces the adhesion of particles and/or liquid to the surface thereby in effect repelling such materials. The substrate is preferably an aromatic polycarbonate sheet or a multi wall polycarbonate sheet that is utilized in glazing applications but is also applicable for opal white or bronze thermoplastic sheet. The coating also has a ultraviolet light (UV) absorber and may also comprise a mar resistant additive.

This invention also relates to the coating compositions useful for making the sheets of the invention.

BACKGROUND OF THE INVENTION

For buildings in certain areas, there is a definite need for easy self-cleaning properties for thermoplastic glazing, particularly polycarbonate clear sheets used in glazing applications. Self-cleaning may occur by rain water running over the surface of a sheet. Easy self-cleaning is important in order to maintain high light transmission properties of transparent or translucent sheet and to minimize build up of unwanted materials on the surface of the sheet. This would also dramatically lower the frequency of cleaning roofing or glazing in buildings, covered walkways, conservatories and the like. This would also be advantageous for decorative translucent thermoplastic sheet such as opal white or bronze thermoplastic sheet.

Therefore, the instant invention is directed to a novel coating system for sheets, and more particularly polycarbonate sheets, utilized in glazing applications wherein the coating system greatly reduces the adhesion of liquids and/or solid particles (dirt) to the surface of the thermoplastic sheet thereby making the sheet easily cleanable by washing or self cleaning by rain water and the like.

SUMMARY OF THE INVENTION

The coating compositions of the instant invention may be employed in combination with additional UV protective coatings as well as primers for hardcoat or mar resistant coatings such as silicone hardcoats that contain colloidal silica. If a sufficient amount of UV light absorber is incorporated in the coating with the repelling additive no additional coating is required for UV protection. Similarly it is possible to improve mar resistance of the surface of the sheet either by incorporating in the coating with the repelling additive a mar resistant additive or by applying an additional coating with a mar resistant additive.

The coating system of this invention contains as repelling additive a silicone modified polyacrylate, preferably a hydroxy-functional silicone modified polyacrylate and a UV light absorber that is compatible with the repelling additive. When a mar resistant additive is incorporated in the coating with the repelling additive this should also be compatible with the repelling additive. The coating system will be applied to transparent or translucent substrates like thermoplastic sheets and the like. However, the preferred substrate is a transparent or translucent polycarbonate sheet or polycarbonate multiwalled sheet comprising at least two polycarbonate sheets having interposed there between a thermoplastic corrugation or web or the like structure separating but joining the at least two polycarbonate sheets. Transparent and translucent is defined in the context of this invention as meaning a light transmission of visible light of at least 10 %, more preferably at least 40%. If the coatings are applied separately, the coating with the UV light absorber may be employed as a primer for a silicone hardcoat coating.

While many different UV additives may be employed in the practice of one aspect of this invention, a preferred UV protective coating is disclosed in US Patent 5,869,185 and a preferred hard coat is disclosed in US Patent 4,373,061 the disclosures of which are incorporated herein by reference. The preferred UV absorber that may be employed herein as disclosed in US 5,869,185 is a polybenzoylresorcinal such as 4,6-di-(4' – t – butylbenzoyl) resorcinol or 4,6 – dibenzoyl – 2 – propylresorcinol. The hard coat preferably comprises a colloidal silica silicone.

BRIEF DESCRIPTION OF THE DRAWING; Brief description of the results obtained with the invention.

When a polycarbonate multiwall sheet (MWS) without the inventive coating such as the commercially available Lexan® Thermoclear® sheet is stained with a red pigment, the pigment sticks to the surface of the sheet and can not be washed away by water running over the sheet. When the MWS is provided with the inventive coating the pigment is almost completely removed by running water. This is shown in Figures 1 A and 1 B respectively.

When some oil is applied on the same sheets as described above, the oil on the sheet of the invention contracts after one minute into oil droplets. On the commercially available product the oil remains smeared out. This is shown in Figures 2B and 2 A respectively.

The contact angle of a droplet of water on the commercially available MWS sheet is about 66°; on the sheet of the invention about 101°. See Figures 3 and 4 respectively.

DETAILED DESCRIPTION OF THE INVENTION

The instant invention is directed to a coating to be applied to a substrate, preferably a thermoplastic sheet and more particularly a polycarbonate sheet which is preferably a clear polycarbonate sheet or a multiwalled polycarbonate sheet wherein at least two sheets having interdisposed there between a structure joining the least two sheets. The interdisposed structure may be for instance a thermoplastic corrugation, a web, a diamond shape structure or the like. The structure may be of the same or different thermoplastic resin than the thermoplastic sheets having said structure interdisposed there between.

As stated previously, the adhesion reducing additive of this invention, which may also be referred to as a repellant to liquids and solid particles (dirt), is a silicone modified polyacrylate, preferably a hydroxyl-functional silicone modified polyacrylate that is compatible with any UV absorber such as a polybenzoyl resorcinol as well as preferably being compatible with any mar resistant coating, if employed. Hydroxyl-

functional silicone modified polyacrylates are commercially available. They are recommended for incorporation in paints as surface additive to improve ease of surface cleaning. According to a datasheet of a supplier of the additive they can be used in the following binder systems: two pack-polyurethanes, alkyd-melamine, polyester, melamine, acrylic-epoxy combinations and phenolic resins. The coating comprises in combination with the adhesion reducing additive (the silicone-modified polyacrylate), a UV resistant additive; it may further comprise a mar resistant coating. The substrate can be coated with several different coating compositions. Each coating composition may be applied as a separate coating wherein each coating is either cured or dried first before any subsequent coating is applied. If separate coatings are applied, it is preferred that the adhesion reducing coating be applied last such that it is the outermost coating. Preferably, however, all three ingredients are incorporated into one coating thus avoiding the additional steps with applying separate coatings.

The reduced adhesion additive may be employed in concentrations and in particular in concentrations that would not effect the excellent light transmission of a transparent or clear thermoplastic substrate while still providing reduced adhesion or repellant properties. Generally, the light transmission of a transparent thermoplastic sheet is between 64 to 84% and higher depending on the thickness of the thermoplastic substrate. Preferably, the concentration of the silicone modified polyacrylate is about 0.5 to about 15.0, more preferably 0.5-10% by weight based on the total weight of the coating to be applied to the thermoplastic substrate. While not intending to be bound by this theory, the self cleaning effect of the repellent is known as the Lotus effect which is based on the self cleaning ability of a Lotus flower to cleanse itself of dirt and/or water due to the surface roughness caused by different microstructures together with hydrophobic properties of the chemical substances in the micro layer of the Lotus flower. Thus the adhesion of water and particles is greatly reduced.

The adhesion reducing additive or repellant is a silicone modified polyacrylate that is compatible with the UV light absorber additive; the UV light absorber additive (sometimes designated as UV resistant additive) can be of any known type: it is preferably a polybenzoyl resorcinol. The repellant of this invention should preferably be compatible with any mar resistant additive or hard coat employed in the practice of

this invention. Any UV resistant additive and the repellant should preferably be employed with a transparent polymer matrix such as an acrylate or methacrylate polymer or copolymer thereof as a binder for the additives in combination with a solvent such as methoxy propanol. Such acrylate or methacrylate polymers or copolymers preferably comprise at least 75 %, more preferably at least 90 % by wt. of the (meth)acrylate with respect to the total amount of polymeric binder in the coating. Therefore, the coating composition may comprise the novel repellant of this invention, a UV resistant additive and/or a mar resistant additive all in combination with an (meth) acrylate base polymer matrix and a solvent.

The polymer matrix is present in an amount of about 10 to about 30% by weight based on the total weight of the coating composition. The UV resistant additive may range from about 2 to about 6% by weight based on the total weight of the coating composition. The additives may vary in the amounts set forth above providing the amounts employed are compatible and do not substantially effect the light transmission of the transparent or translucent thermoplastic sheet and preferably not below about 40% light transmission.

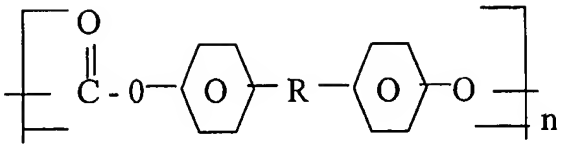
Compatible or compatibility, as used throughout this application, is defined as meaning a composition wherein phase separation of the additives from the polymer matrix is not prominent upon inspection with the naked eye.. The transparent polymer matrices should be compatible with the UV resistant additive particularly the polybenzoylresorcinol described herein and in US Patent 5,869,185. Examples of the transparent polymer matrices that may be employed herein beside an acrylate or methacrylate polymer include polyurethanes, polycarbonates, polystyrenes, or copolymers as well as mixtures thereof. As used herein, acrylate polymers may be defined as acrylates, methacrylates as well as copolymers and mixtures thereof. Included in the term coating composition are compositions that typically and preferably comprise acrylate polymers and an organic solvent as well as emulsions of acrylate polymers and water and acrylate polymer compositions in water. When an organic solvent is employed, it should be of the type that dissolves the acrylate polymer, is inert towards the substrate particularly a thermoplastic substrate, and which organic solvent is readily volatized. Some non limiting examples of such

solvents include hydroxyethers, alcohols, beta alcohols, liquid aliphatic hydrocarbons and mixtures thereof. A preferred organic solvent is methoxy propanol.

If a mar resistant additive is employed, there is no limitation of the type of mar resistant additive other than it adheres to the coating/primer. However, a preferred mar resistant additive is a colloidal silica silicone hardcoat. The UV resistant additives particularly the polybenzoylresorcinols also serve as primers for silicone hardcoats.

The substrate employed in the practice of this invention may be any substrate such as opaque or clear thermoplastic substrates such as opal white, bronze or transparent substrates. In one embodiment, the substrate is a thermoplastic substrate. In another embodiment, the substrate is selected from not limited thereto, the group of, carbonate homopolymers; polyester carbonate copolymers obtained from the reaction product of a dihydroxy phenol, a carbonate precursor and a dicarboxylic acid such as terephthalic and/or isophthalic acid; blends of polycarbonate with other polymers; acrylates; methacrylates and copolymers; styrene polymers; polysulfones; mixtures thereof; and the like.

The thermoplastic substrate may be a single sheet or a laminated sheet of at least two sheets or a polycarbonate composite multiwalled glazing sheet known as Lexan® Thermoclear®, manufactured and sold by General Electric Company's Plastics component. The preferred substrate is a polycarbonate sheet or a polycarbonate composite or Lexan® Thermoclear® (MWS). MWS is a multiwall polycarbonate transparent sheet extruded from polycarbonate resin and comprises at least two polycarbonate sheets having interdisposed and joining said sheets a structure that may be a web, corrugation, diamond or just rib configuration. The polycarbonate resin is an aromatic carbonate homopolymer made up of recurring aryl polycarbonate units of the formula:



wherein R is a divalent hydrocarbon radical containing from 1 – 15 carbon atoms and n is an integer of from about 20 to about 150. The polycarbonate is obtained by the reaction of an aromatic dihydroxy compound with a carbonate precursor such as a carbonyl chloride or a diaryl carbonate or the like. A preferred aromatic dihydroxy compound is 2, 2 – bis (4 – hydroxy phenyl) propane also commonly known as Bisphenol – A.

The long term maintenance of the repelling properties of the sheet of the invention can be enhanced by incorporating in the coating composition cross linking agents such as isocyanates.

EXAMPLES The following Examples are provided merely to show one skilled in the art how to apply the principals of this invention as discussed herein. The Examples are not intended to limit the scope of the claims appended to this invention.

Example 1. Polycarbonate multiwall sheets namely Lexan® Thermoclear® sheets (MWS) were coated with just a UV resistant protective coating 4, 6 – dibenzoylresorcinol as a control sample (4.5% by weight) and a MWS sheet coated with the same UV resistant coating having added to the coating composition the adhesion reducing additive (AR) of the invention. The amount of UV resistant additive employed was about 4.5% by weight and about 2% by weight of the adhesion reducing additive, namely a hydroxy-functional silicone modified polyacrylate. The coating composition also contained in combination about 20% by weight of poly methyl methacrylate polymer matrix with the balance being about 73.5% by weight of methoxy propanol solvent. The weight percents are based on the total weight of the coating composition. With each specimen, the contact angle of a drop of the

specimen was measured (shown in Figures 3 and 4). The results obtained are set forth in the following Table 1.

TABLE 1

Test Liquid	Contact Angle Control	Contact Angle Adhesion Reducing Additive
Water	66°	101°
Glycerin	40°	101°
Ethyleneglycol	50°	91°
1-Octanol	13°	18°
M-Dodecane	10°	12°

As shown by the test results in Table 1, the addition of the adhesion reducing additive greatly increases the contact angle of a bead of the liquid with the surface of the substrate. The greater the angle of contact, the less is the adhesion of the liquid to the substrate surface, and thus easier to remove with water or washing. The contact angle of a bead of liquid with respect to the control sample and a sample of the additive of the instant invention have also been described here above.

Example 2. The samples prepared in Example 1, namely the Control sample and the sample of this invention were measured for surface tension, disperse part and polar part. The results obtained were as follows:

TABLE 2

Sample	Surface Tension mN/m	Disperse Part*	Polar Part*
Control	38.2	20.7	17.5
Adhesion Reducing Additive	21.9	21.5	0.4

m N/m means – milli newton/meter

*Corresponding with the basic interaction forces, the Adhesion energy can be divided in a polar part and a disperse part. First part is based on London forces also known as van der Waals force and occurs on every interface between liquid, gas and solid surfaces. For the second part, polar molecules are needed. The surface energy can also be divided into a disperse and a polar part: sigma (i) = sigma (i) disperse + sigma (i) polar. In order to calculate both parts separately the assumption is made that various disperse surface energies add up to one part of disperse adhesion energy and for polar part. Adhesion energy means the energy that is needed to remove for instance the liquid droplet from the solid substrate. This is dependent on the contact angle, the lower the contact angle the higher the adhesion energy and the higher the contact angle the lower the adhesion energy.

The results show that the surface tension of the liquid bead was significantly lower than the control sample, further demonstrating that the tendacity of the liquid to the substrate surface is greatly reduced. A higher dispersed part and a lower polar part is wanted for lower surface tension thereby again demonstrating that the liquid is easier to remove from the substrate surface due to lower surface tension.

Example 3. Lexan® Thermoclear® substrate samples without and with a coating of the repellent of this invention were stained with a red pigment build up. The samples were then cleaned with water. The results are also described above; the red pigment build up is easily removed with water from the sample having a coating containing the adhesion reducing additive of this invention.

Example 4. Lexan® Thermoclear® substrate sample is coated with the repellent of this invention. Oil is placed on the surface of the sample. Oil is also placed on a control sample having no coating. The results are also described above. After 1 minute the oil has not dissipated on the control sample while on the coated sample employing the repellent of this invention, the oil is almost repelled after 1 minute.

Example 5. Polycarbonate multiwall sheets namely Lexan Thermoclear(R) MWS were coated with the same coating composition as in example 1 and. MWS sheets coated with the same UV resistant coating having added to the coating composition

additional amounts of the same adhesion reducing additive (AR) to increase concentration to 6% and 10% with the aim to improve contact angle retention after artificial, weathering.

Table 2

AR (% wt.)	Contact angle	
	Before weathering	After weathering
2%	66°	71°
6%	___	87°
10%	___	91°

The weathering test was performed in this example and all following examples for 1500 hours in a Atlas weatherometer in accordance with ISO 11341 with a Xenon light source with 300-400 NM 50W/m^2 at a chamber temperature of 40 ° C and a relative humidity of 70 %. The light was constantly switched on and the spraying was alternately switched on (18 minutes) and off (102 minutes). The equipment was provided with a CIRA inner filter and a Sodalime outer filter.

As shown by the test results in Table 2, the increased level of the adhesion reducing additive greatly increased the contact angle of water after artificial weathering maintaining the easy clean effect for longer times in service.

Example 6. Polycarbonate MWS were coated with the same coating compositions as described in example 5 comprising additionally 1, 3 or 5% by weight of an aliphatic polyisocyanate (Cas# 28182-81-2) to further retain the contact angle after artificial weathering.

Table 3

AR level	Isocyanate level	Contact angle after 1500 hrs weathering
2%	0%	71°
6%	0%	88°
10%	0%	91°
2%	1%	80°
6%	3%	85°
10%	5%	91°

As shown by the test results in Table 3, the addition of the polyisocyanate further increases the contact angle of water after artificial weathering maintaining the easy clean effect for longer in service.

Example 7. Polycarbonate MWS were coated using coatings as described in example 1 but incorporating about 6% of an alternative UV absorber namely 2-hydroxy-4-octyloxybenzophenone, Cas # 1843-05-6, with AR additive levels and polyisocyanate as described in examples 5 and 6.

Table 4

AR level	Isocyanate level	Contact angle after 1500 hrs weathering
2%	0%	75°
6%	0%	84°
10%	0%	89°
2%	1%	79°
6%	3%	89°
10%	5%	98°

The results of table 4 show similar trends with further improvements to example 6.

Although this invention has been described by reference to particular illustrated embodiments thereof, many variations and modifications of this invention may become apparent to those skilled in the art without departing from the spirit and scope of this invention as set forth in the appended claims hereto.

What is claimed is:

1. A transparent or translucent sheet comprising a substrate having on an outer surface facing the atmosphere a coating with a composition comprising a hydroxy-functional silicone modified acrylate polymer repelling additive in an amount sufficient to allow ease of removing solid particles and liquids on said surface by reducing the adhesion of such particles and liquids to the substrate and a ultraviolet light absorber.

2. The sheet of claim 1 wherein the coating as applied in the process of manufacture of the sheet has a composition comprising about 0.5 weight % to about 15.0 weight % of the repelling additive based on the total weight of the coating composition.

3. The sheet of claims 1-2 wherein the coating as applied in the process of manufacture of the sheet has a composition comprising about 0.5 to about 10.0 percent by weight of the ultra violet light absorber based on the total weight of the coating composition.

4. The sheet of claims 1-3 wherein the coating further comprises a polymer matrix selected from the group consisting of transparent or translucent polyurethanes, polycarbonates and copolymer thereof, polystyrene and copolymers thereof, acrylate and methacrylate polymers and copolymers thereof and mixtures thereof.

5. The sheet of claim 4, wherein the polymer matrix is an acrylate or methacrylate polymer or copolymer.

6. The sheet of claims 1-5, wherein the coating further comprises a mar resistant additive.

7. The sheet of claim 6 wherein the mar resistant additive is a colloidal silica silicone hard coat additive.

8. The sheet of claims 1-7 wherein the substrate is made out of an aromatic polycarbonate, an acrylic resin or a polyestercarbonate resin. .

9. The sheet of claims 1-8 wherein the substrate is a multiwalled composite consisting essentially of at least two layers and there between a structure joining the at least two layers and wherein the multiwalled composite is transparent.

10. Coating composition suitable for manufacture of the transparent or translucent sheet of claims 1-9 comprising a polymer matrix material, a hydroxy-functional silicone modified acrylate polymer repelling additive, an ultraviolet light absorber and an organic solvent for the polymer matrix.

11. The composition of claim 10 further comprising a mar resistant additive.

FIG. 1A

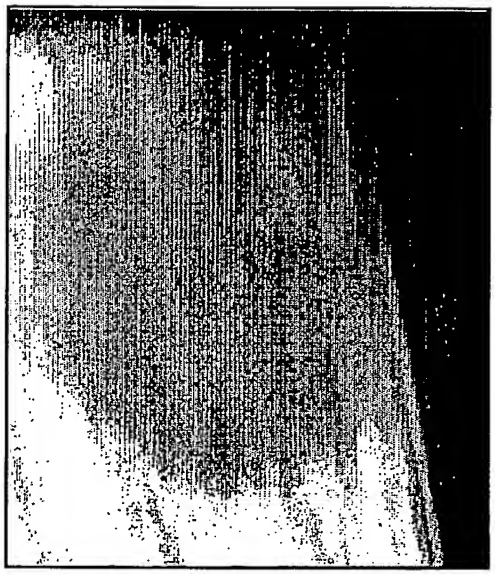


FIG. 1B

FIG. 2B

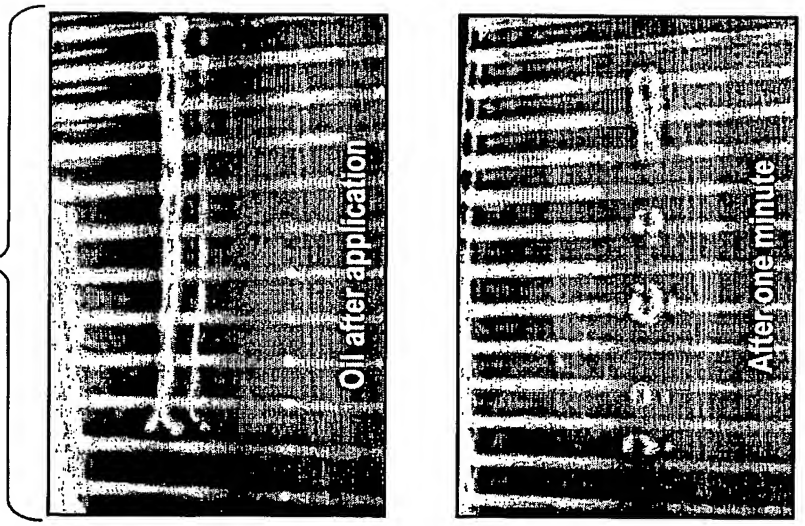

Oil after application
After one minute

FIG. 2A

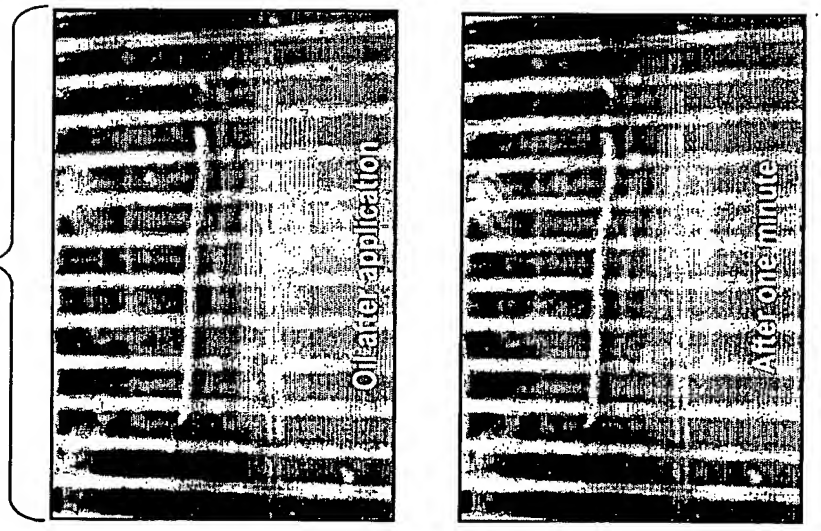

Oil after application
After one minute

FIG. 4A

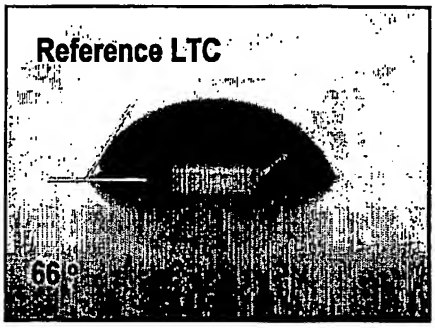
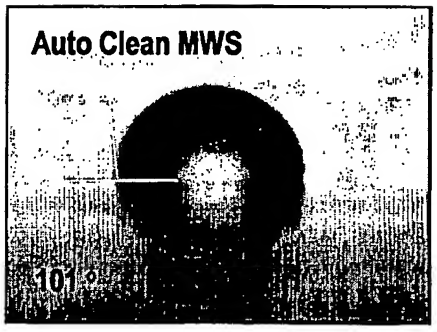


FIG. 4B



INTERNATIONAL SEARCH REPORT

Int nal Application No
PCT/US 02/41187

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J7/04 C09D7/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 439 293 A (DOW CORNING) 31 July 1991 (1991-07-31)	1,3,6-8
Y	claims 1,5 page 5, line 24 - line 38 page 6, line 31 - line 40 examples 2,3	1-11

X	US 6 054 534 A (SILBER STEFAN ET AL) 25 April 2000 (2000-04-25)	11,12
Y	claims 1,5,7-9 column 1, line 56 - line 61 column 4, line 1 - line 7 column 4, line 38 - line 46 column 4, line 58 - line 62 column 6, line 37 - line 52 column 8, line 3 - line 17	1-11

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
16 April 2003	14/05/2003

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int al Application No
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